

# Liquid Hydrogen Infrastructure Analysis

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# Overview

## Timeline and Budget

- **Start date:** January 2017
- **End date:** December 2017
- **% Complete:** 5%
  
- **FY16 DOE funding:** \$50k
- **FY17 DOE funding:** \$190k
- **Total DOE Funds Received to date:** \$240k

## Barriers

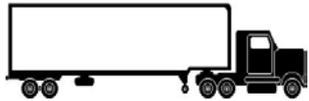
- **A. Lack of Hydrogen and Infrastructure Options Analysis**
- **C. Reliability and Costs of Hydrogen Pumping**

## Partners/Collaborators

- **LLNL (lead)**
- **Linde:** LH<sub>2</sub> pump operation & maintenance, LH<sub>2</sub> delivery
- **BMW:** LH<sub>2</sub> pump operation
- **Argonne National Lab:** H<sub>2</sub> infrastructure, interface with HDSAM

# ***Relevance* : Liquid hydrogen (LH<sub>2</sub>) has many benefits for the hydrogen infrastructure, especially at large scale(s)**

- High density LH<sub>2</sub> allows minimum volume & mass per kg H<sub>2</sub>, thus *minimum* cost
- High capacity per truck & short transfer times *minimize* delivery logistics/scheduling
- *Low* potential burst energy: 20 K and <6 bar vs. 300 K and >200 bar
- LH<sub>2</sub> pumps provide *high* throughputs (120+ kg/hr) at *low* dispensing costs
- High density of LH<sub>2</sub> can be transferred to compact onboard solutions (cryo/cold)



**4,300** kg H<sub>2</sub> capacity  
\$167/kg

LH<sub>2</sub>

From Reddi *et al*, 2015



**800** kg H<sub>2</sub> capacity  
\$783/kg  
**350 bar, composite**



**250** kg H<sub>2</sub> capacity  
\$1000/kg  
**190 bar, steel**

## **Challenges for LH<sub>2</sub>:**

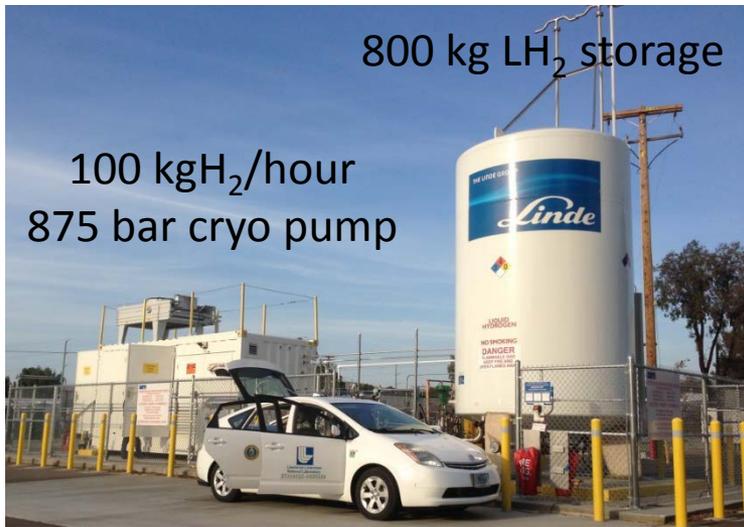
- High cost of liquefaction (~3 X compression)
- Refueling station integration (setback distances limitations)
- Transfer and boil-off losses

Goal of effort: better understand/quantify losses along LH<sub>2</sub> pathway

# Relevance : Cryo-compressed H<sub>2</sub> (CCH<sub>2</sub>) storage exhibits high system densities and affordable cost, that scale well with capacity

	Gravimetric	Volumetric	System cost
700 bar	4.4%	24 gH <sub>2</sub> /L	\$15 / kWh
CCH <sub>2</sub>	7.5%*	45 gH <sub>2</sub> /L*	\$12 / kWh
MOF 5	4%	20 gH <sub>2</sub> /L	\$16 / kWh

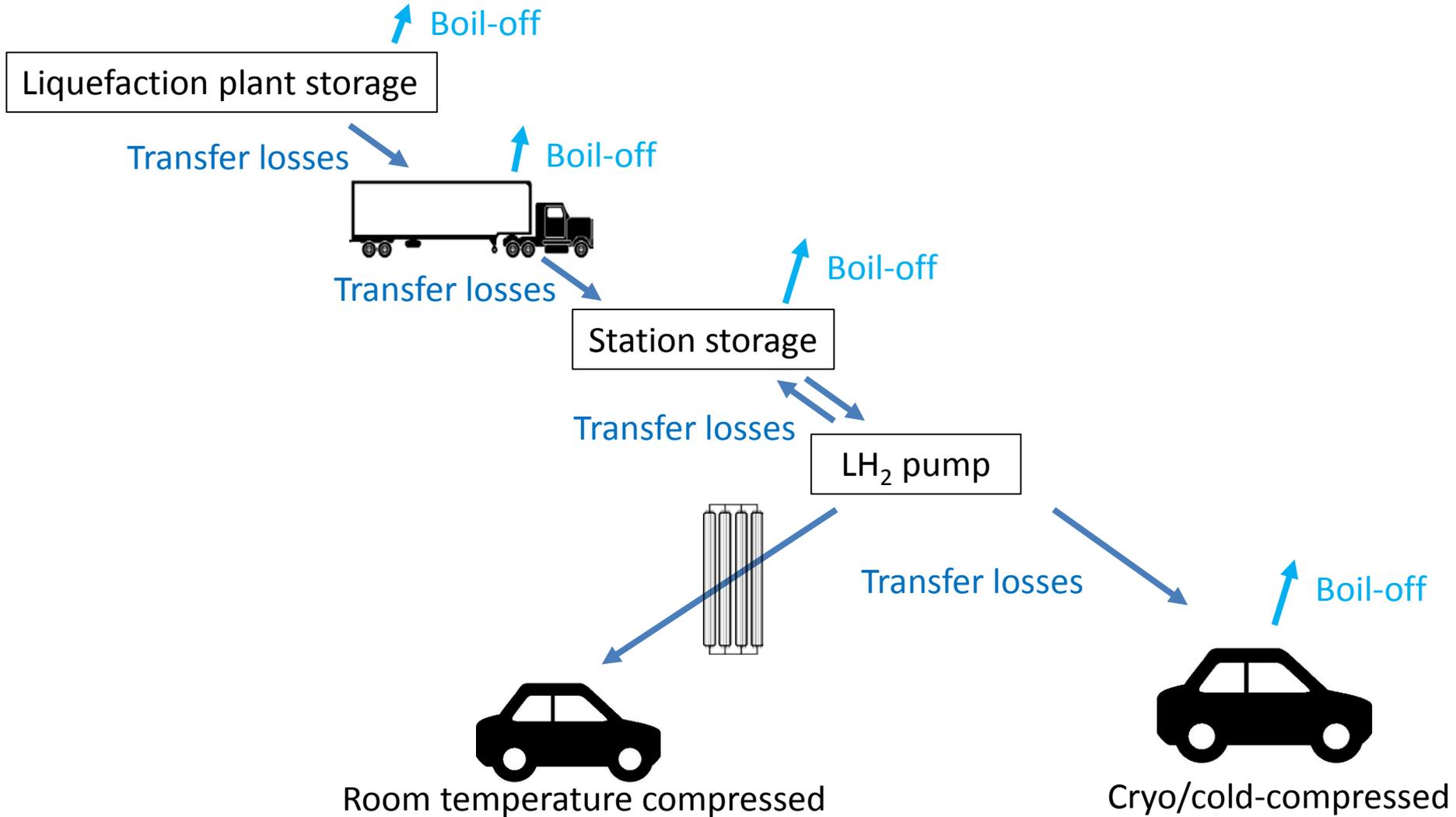
\*demonstrated at LLNL on 10 kg H<sub>2</sub> system



## Challenges for CCH<sub>2</sub>:

- Composite vessel outgassing in vacuum chamber necessitates mitigation
- Material performances at low temperatures not well characterized
- No recognized standards (SAE, ISO..), although CCH<sub>2</sub> mentioned in GTR

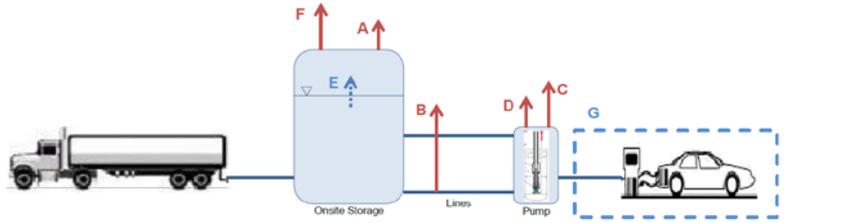
# Approach : Simulate LH<sub>2</sub> pathway using a thermodynamic model to estimate, then mitigate, transfer & boil-off losses



Transfer and boil-off losses occur all along the LH<sub>2</sub> pathway

# Previous work (PD134, Simon) : WTW and emission for CcH<sub>2</sub> pathway

## Approach to estimating potential station boil-off and net losses

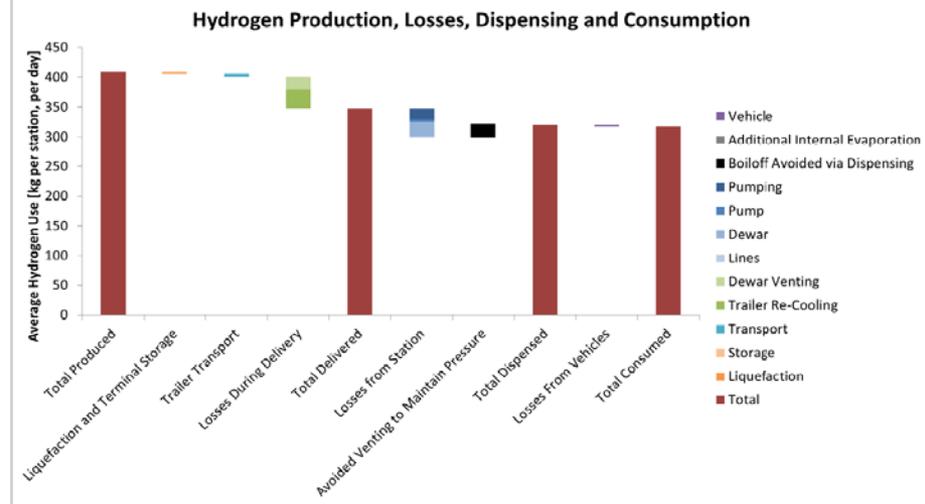


- [A]\* Dewar: 5.5 kg/day for a 725 kg tank.
- [B]\* Lines : 0.3 kg/day per line.
- [C]\*\* Pump: 1.1 kg/day per pump.
- [D]\*\* Pumping: 0.06 kg/kg-dispensed at 700 bar.
- [E] Avoided losses: 0.073 kg H<sub>2</sub> must be evaporated per kg H<sub>2</sub> dispensed.
- [F]\* Delivery losses (cold vapor displacement, bottom-fill): **up to** 0.07 kg vented per kg-LH<sub>2</sub> delivered.
- [G] Station-related losses from the high pressure section are assumed to be zero.

\* Consistent with LLNL's non-optimized tank operation and delivery experience  
 \*\* Consistent with anticipated industrial technology developments

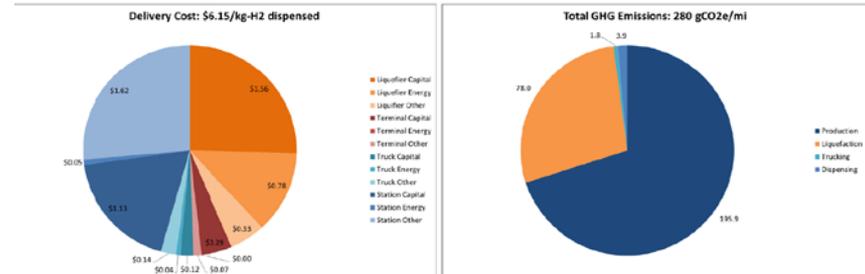


## Accomplishment: Illustrate all potential boil-off losses



## Accomplishment: Cost and Emissions Analysis

- For the analysis depicted below (320 kg/day station), the cost of hydrogen is **\$7.85/kg** and the cost of ownership is **\$0.44/mi**.



Previous work identified H<sub>2</sub> losses based on LLNL setup and evaluated them in the HDSAM framework

# ***Approach* : Simulate LH<sub>2</sub> pathway using a thermodynamic model to estimate, then mitigate, transfer and boil-off losses**

## **Task 1 : Simulate boil-off losses from the liquefaction plant to car dispensing**

- Build/adapt thermodynamic model with real gas EOS and 2 phases for LH<sub>2</sub> pathway
- Evaluate optimal conditions that would minimize boil-off
- Propose improvements to existing procedures/setups

## **Task 2: Simulate on-board losses for cryo-compressed vehicles**

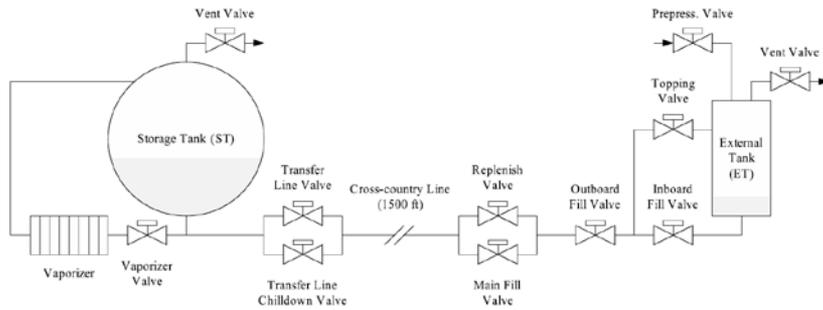
- Gather real-life driving scenarios over a large population
- Build refueling/parking/driving model for cryo-compressed vehicle, including real gas EOS, tank thermal mass, para/ortho kinetics
- Quantify boil-off losses on cryo-compressed vehicles

## **Task 3: Boil-off recovery technologies**

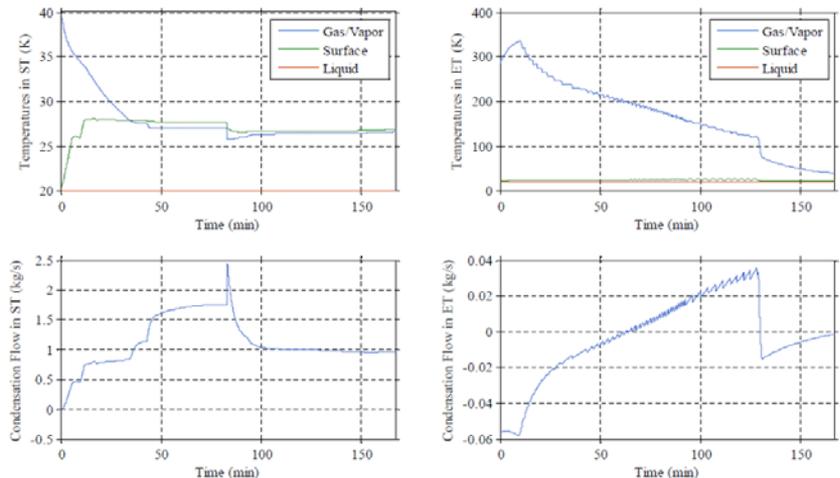
- Identify the source(s) of most significant boil-off along the LH<sub>2</sub> pathway
- Review main boil-off recovery options
- Evaluate costs and performances

Modeling entire LH<sub>2</sub> pathway enables quantitative understanding

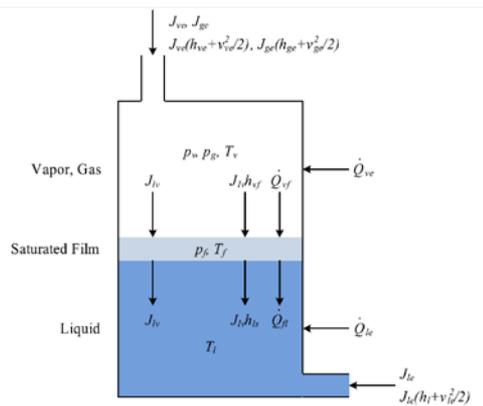
# Approach (task 1) : Simulate H<sub>2</sub> losses from liquefaction plant to car using existing NASA code, written for rocket loading with LH<sub>2</sub>



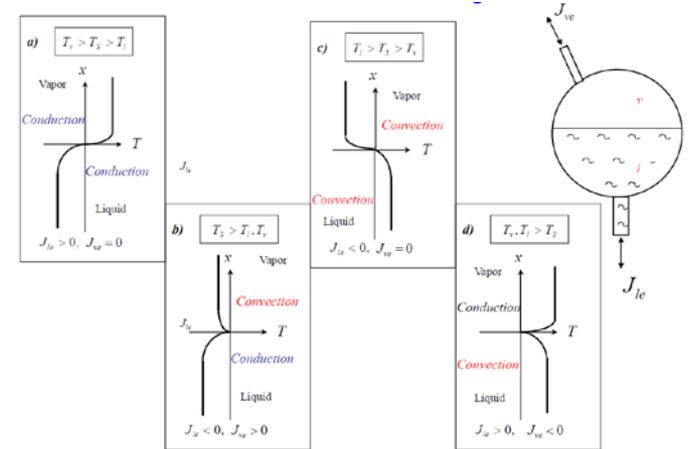
From Osipov and Daigle, 2011



Interaction between two LH<sub>2</sub> volumes and dynamic effects



Condensation/evaporation, energy balance



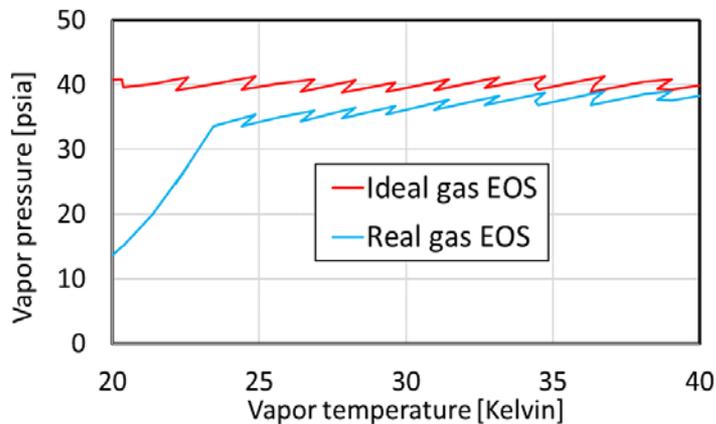
Heat transfer modes with saturated film

Existing code from NASA provides framework for LH<sub>2</sub> transfer analysis

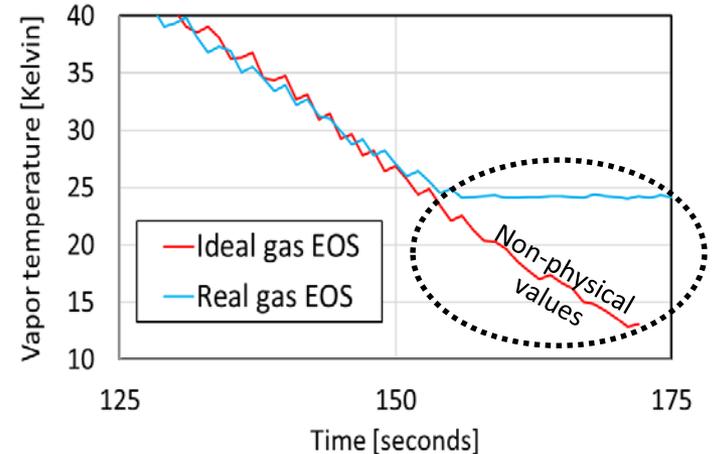
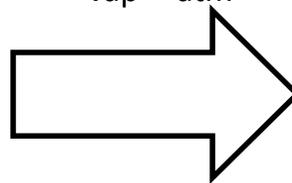
# Accomplishments (task 1) : NASA code is being modified in order to account for specifics of LH<sub>2</sub> infrastructure

## Features to modify/add in original code:

- Real gas EOS, especially single to 2 phase transition for the vapor
- Geometry (tanks size and shapes, valve diameters...)
- Need non-constant liquid temperature, to simulate subcooled conditions
- Update default parameters (heat transfer coefficients, time constants....)
- Top fill into stationary Dewar
- Add return line for pump's storage vessel

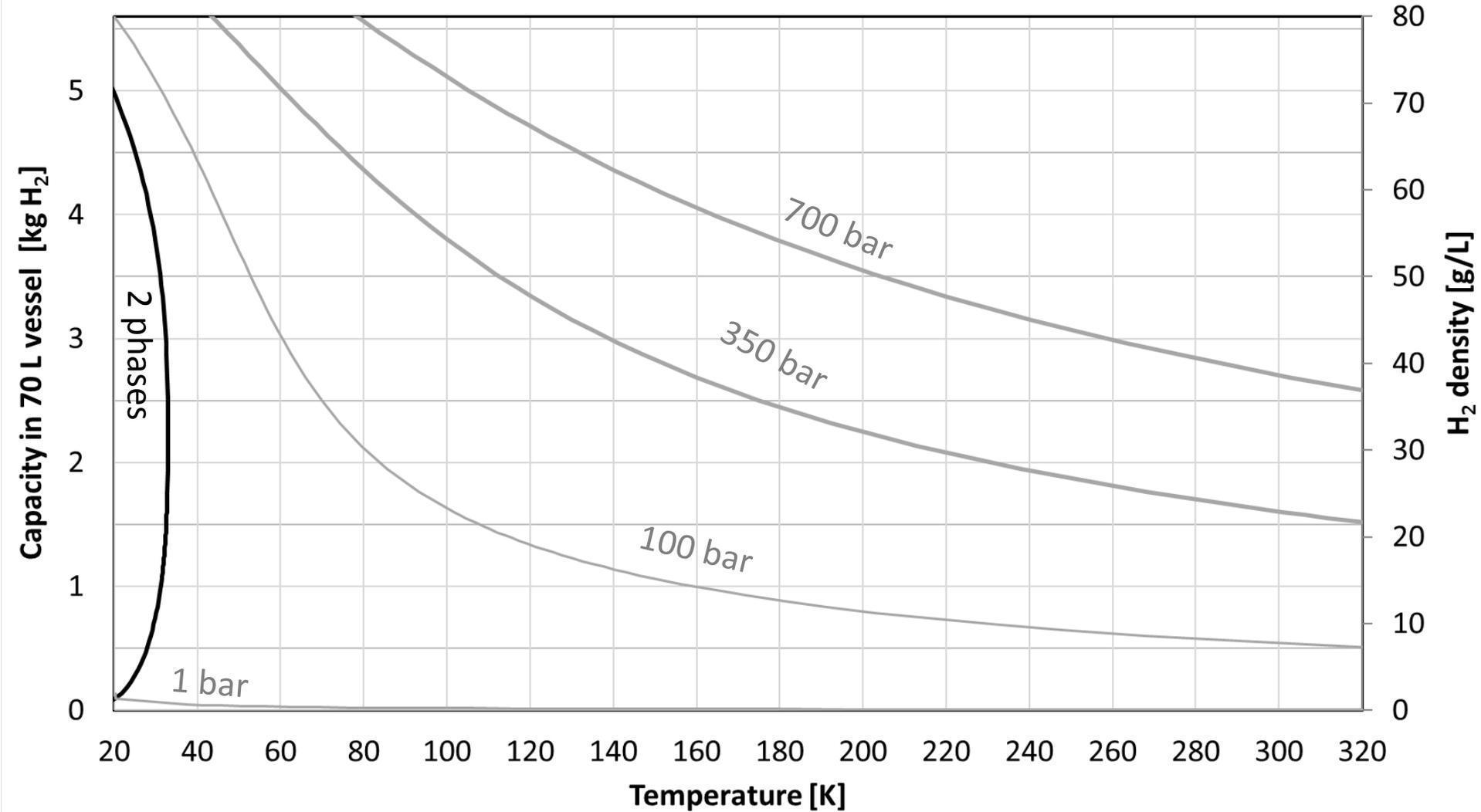


Vapor cooling rate  
function of  
 $\Delta(P_{\text{vap}} - P_{\text{atm}})$

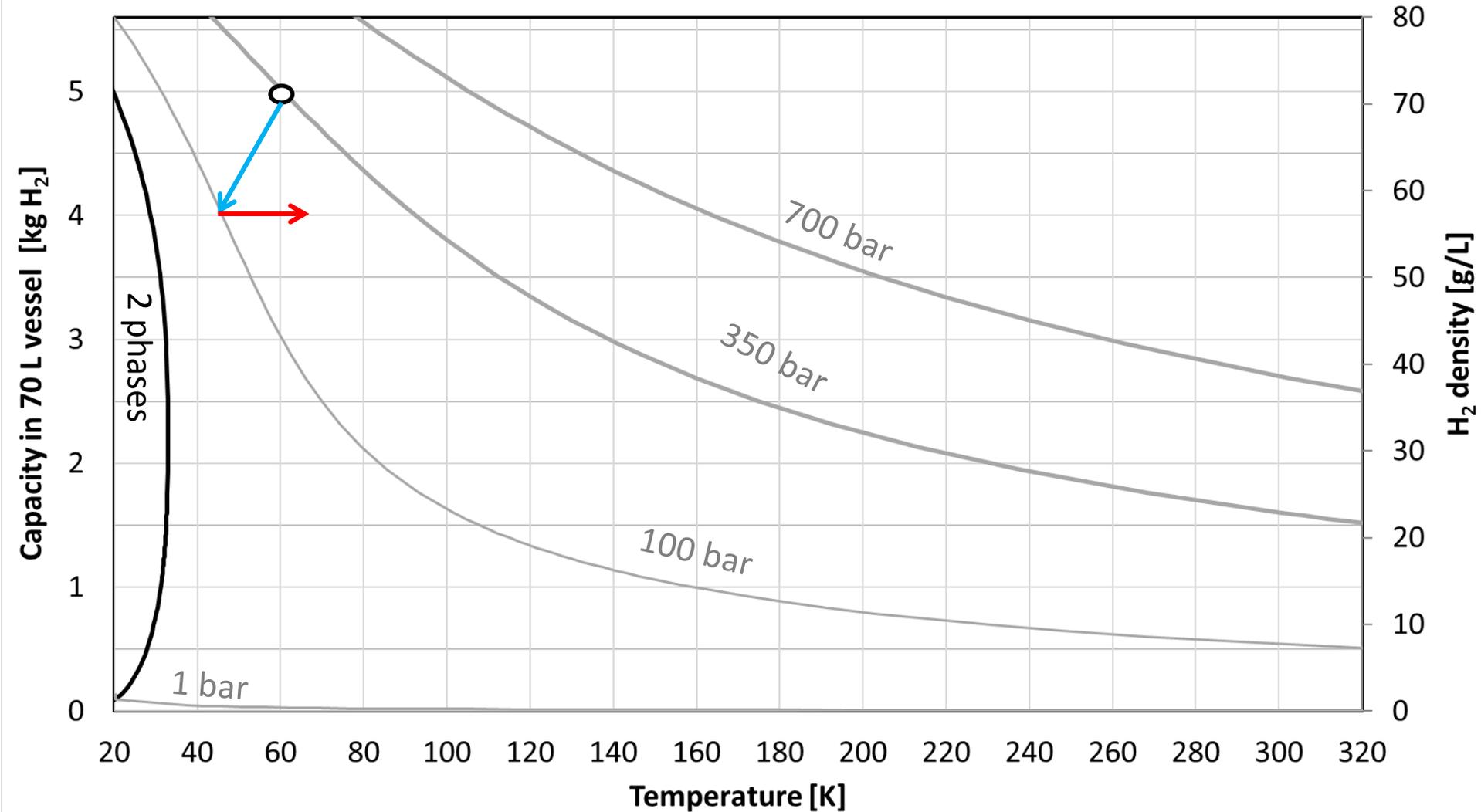


Existing code from NASA will be adapted to our specific conditions

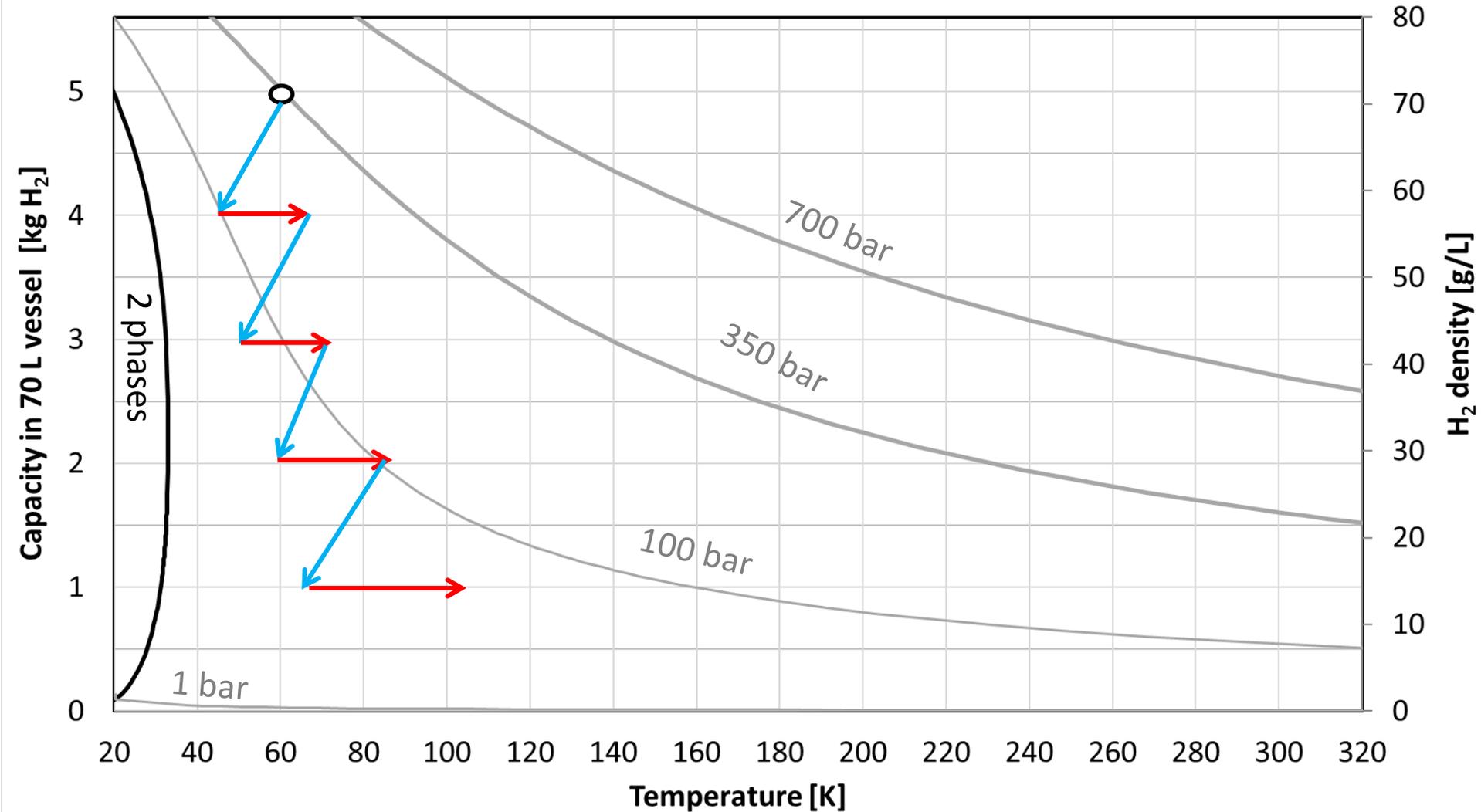
# Approach (task 2): Simulate cryo-compressed vehicle's refueling/driving/parking cycles in order to estimate boil-off losses



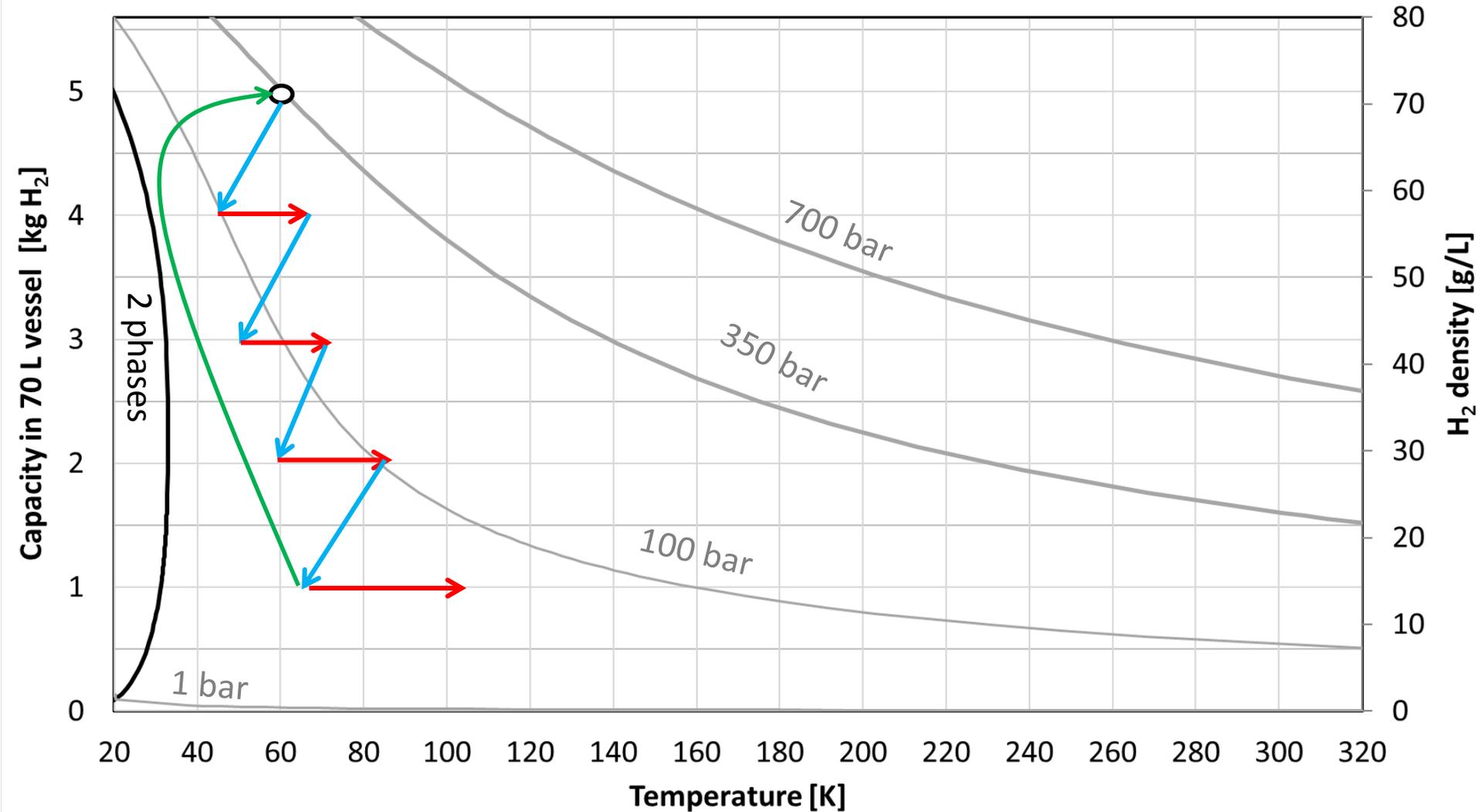
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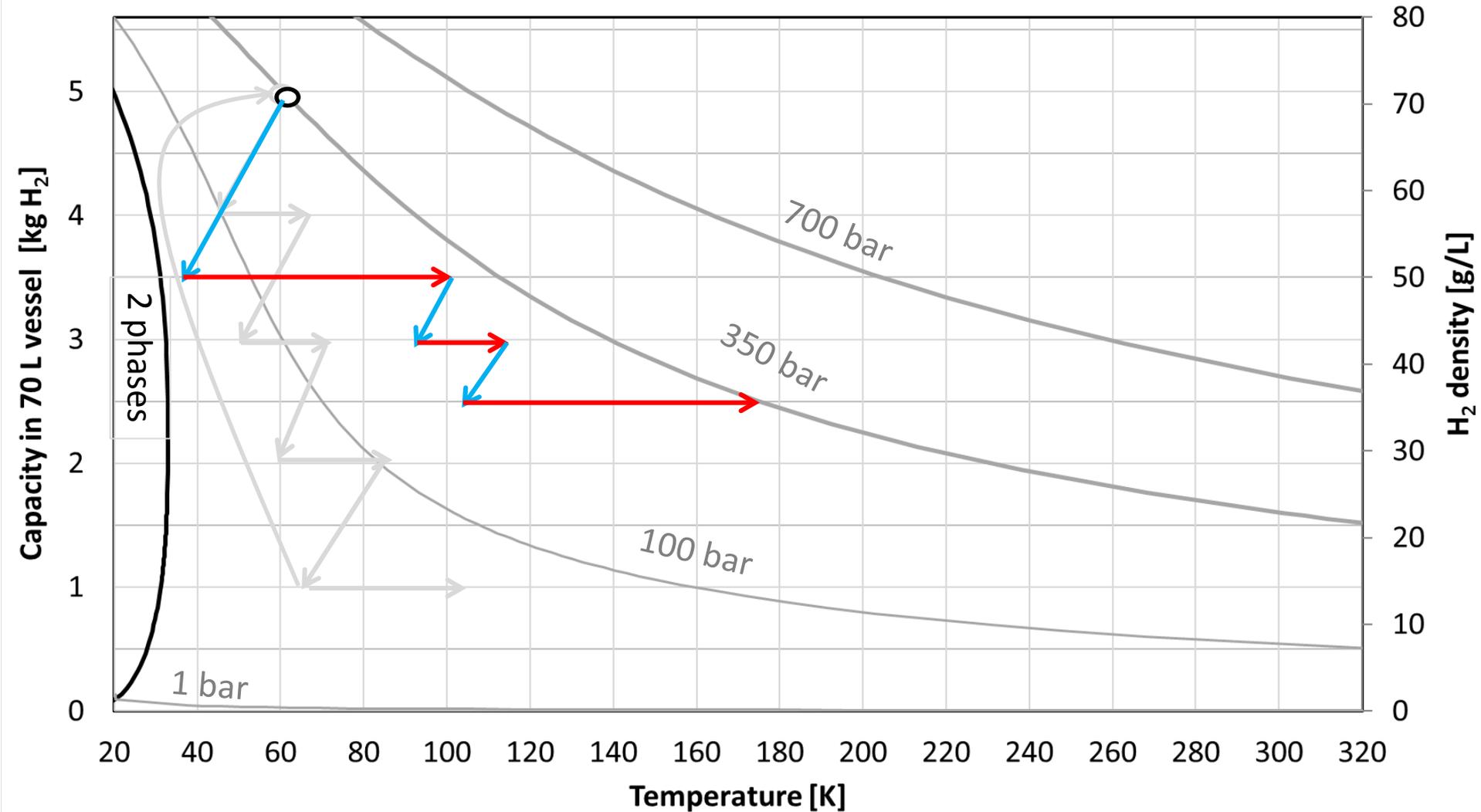
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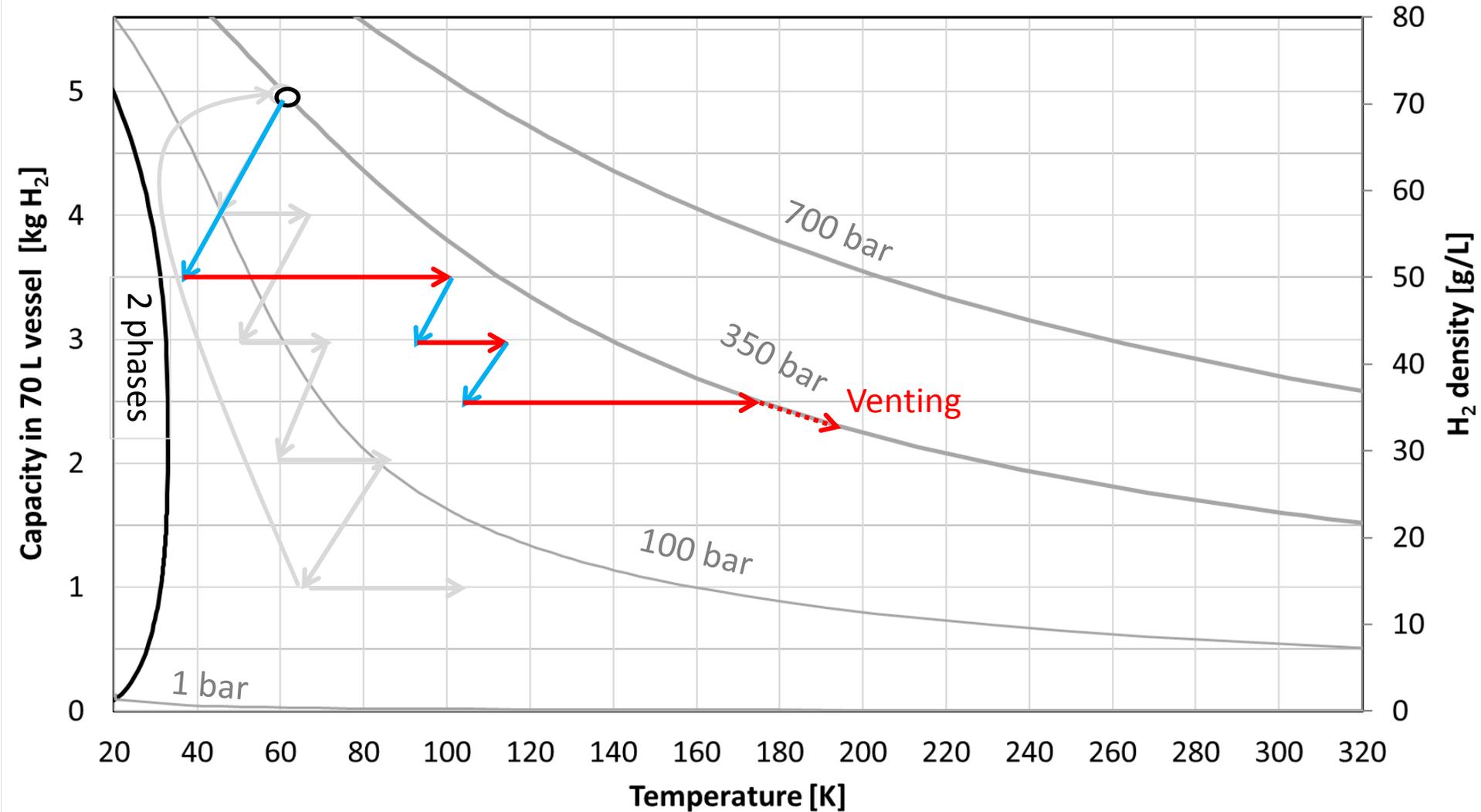
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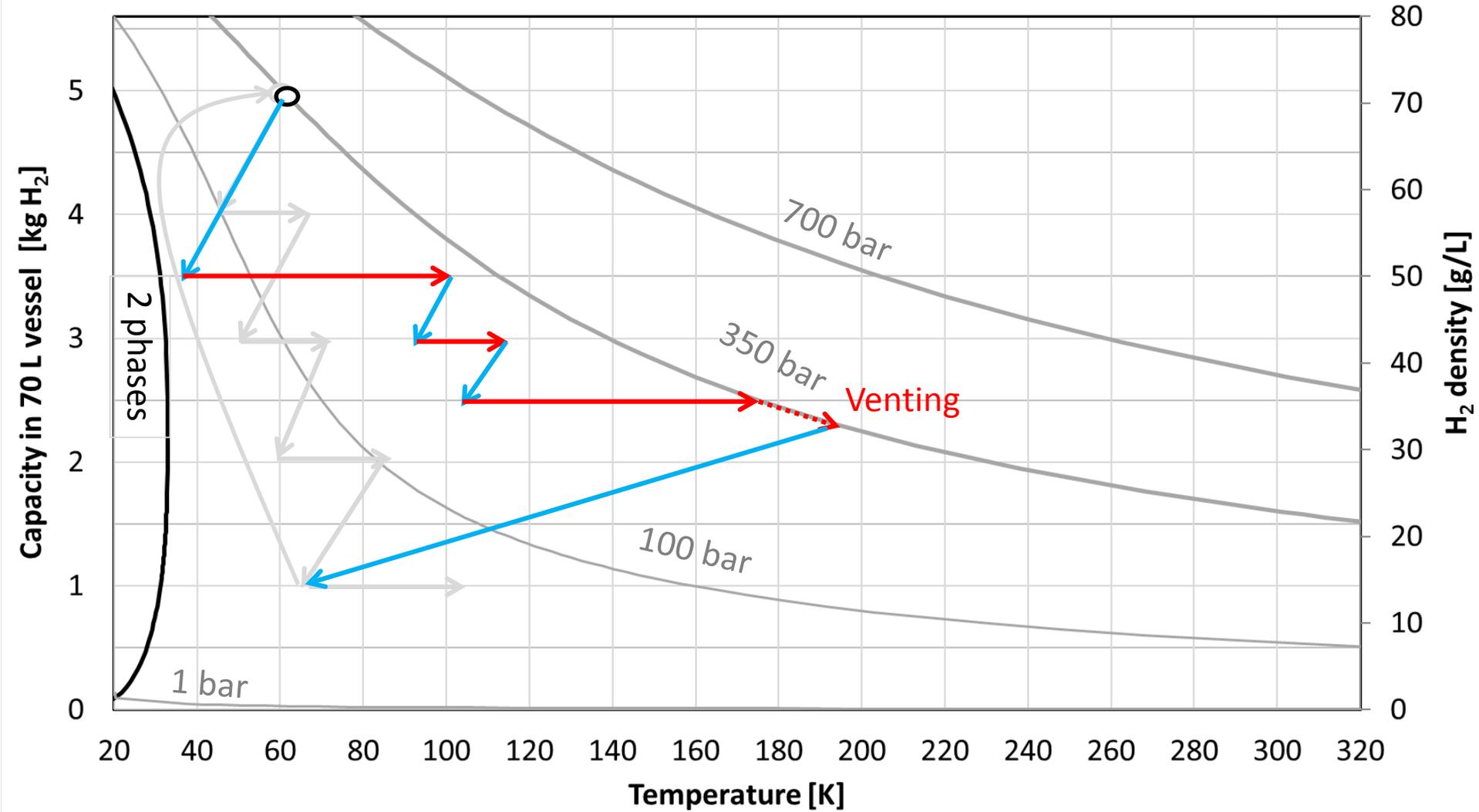
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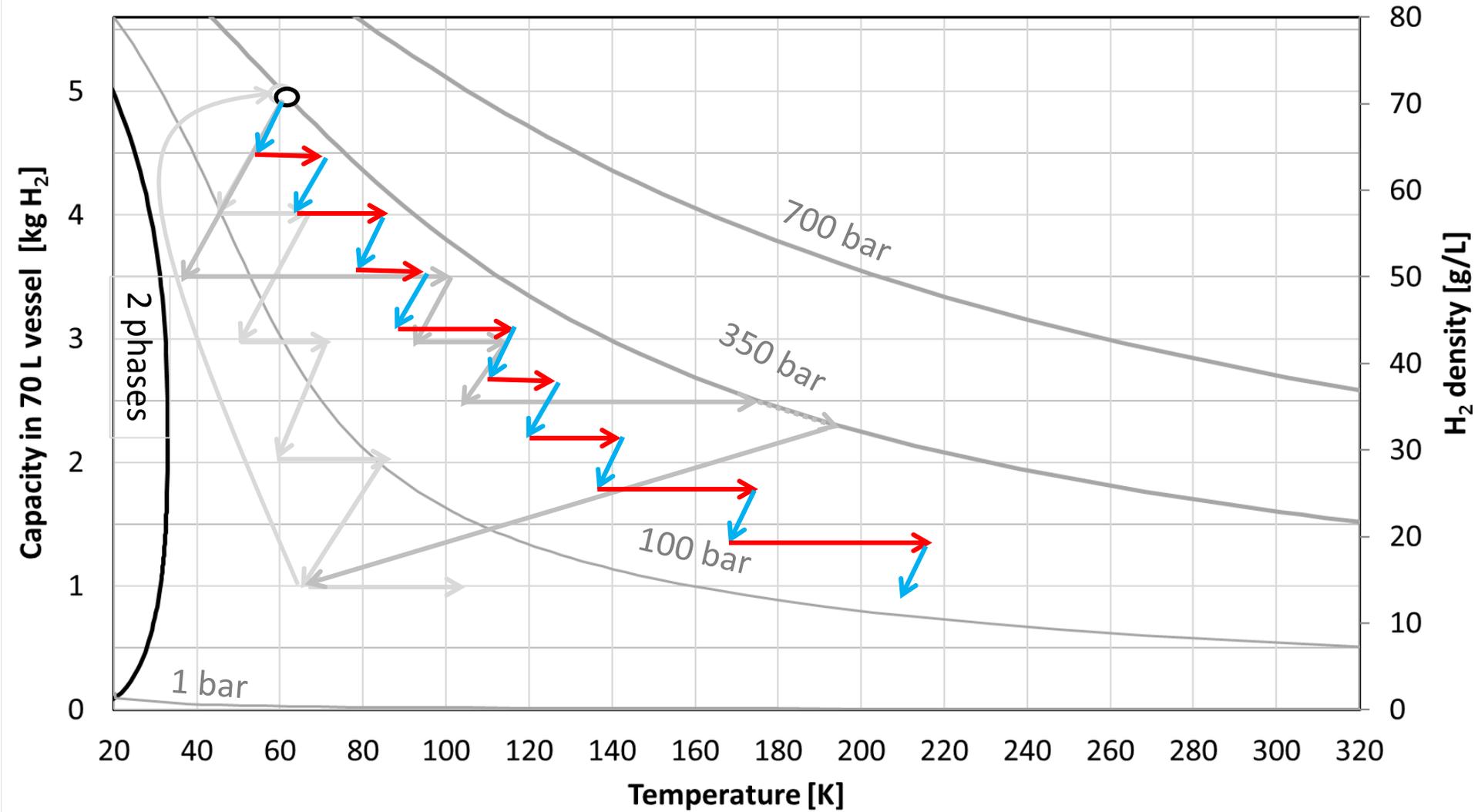
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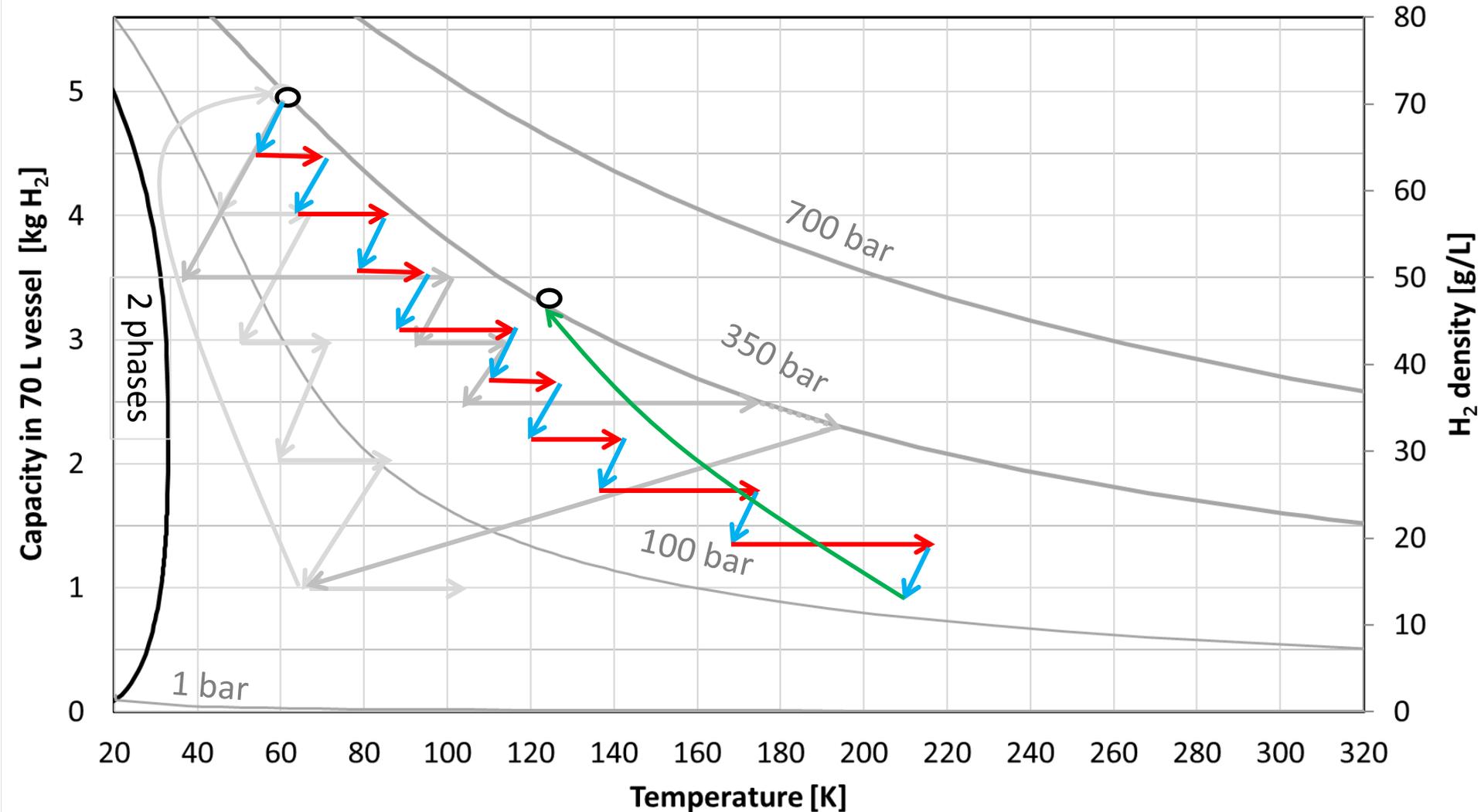
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Influence of utilization patterns on boil-off (and max capacity) will be simulated using a thermodynamic model

## ***Approach (task 2): Simulate cryo-compressed vehicle's refueling/driving/parking cycles in order to estimate boil-off losses***

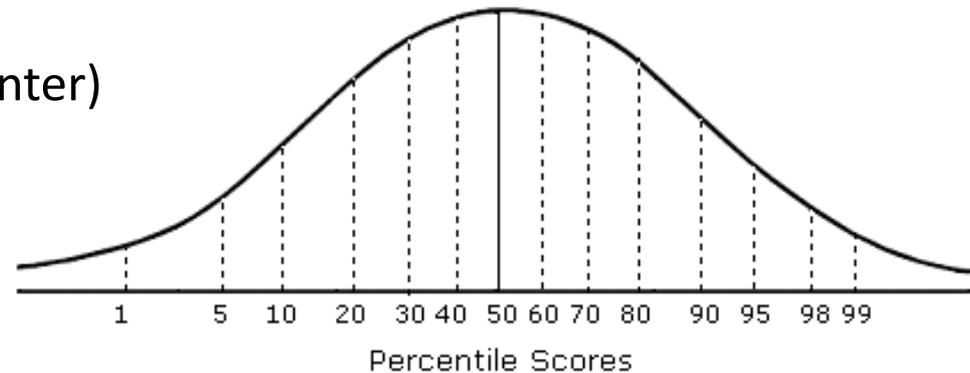
Driving data will be collected in order to simulate boil-off losses of a variety of driving cycle patterns (wide population).

**Key information needed:** parking duration and distance driven, per day.

Both passenger and fleet vehicles are being considered for now.

Sources for driving data:

- California Road Charge Pilot – 9 months, ~5000 users
- UC Davis
- NREL (Secure Transportation Data Center)
- INL (Advanced Vehicles)
- ...



Boil-off losses will be estimated using a statistical approach

## **Approach (task 3) : Identify boil-off recovery technologies/processes that could reduce/eliminate H<sub>2</sub> losses along LH<sub>2</sub> pathway**

Wealth of technologies have been studied by NASA (ZBO concepts).

### **Possible main sources of losses:**

- Trailer depressurization after delivery (50-70 psi to atm)  
*Mitigation: trailer “shake-down”, low entropy LH<sub>2</sub> pump...*
- Station Dewar  
*Mitigation : low footprint compressor (electro-chemical, metal hydride cryo-cooler), fuel cell...*
- Pump Dewar:  
*Mitigation: bottom return recirculation into main Dewar...*
- Vehicle:  
*Mitigation: charge batterie(s), run A/C...*

Different approaches will be analyzed based on flow rates, T and P

# AMR 2016 feedbacks from reviewers (PD134, CcH<sub>2</sub> pathway analysis)

Project is estimating 'potential' boil-off, not necessarily estimating 'actual' boil-off?

Last year's effort was focused on identifying boil-off losses at the CcH<sub>2</sub> station and integrate those results onto HDSAM. FY17 effort is aimed at quantifying those losses.

Not clear if initial description of cryo-compressed is 350 bar or 700 bar. Pressure is not believed to have strong impact at the station level. Both 350 bar (BMW) and 700 bar (LLNL) options are actually investigated through dedicated programs. FY17 effort will address 350 bar only.

Why are "losses from vehicles" after dispensing included in overall boil-off losses? Those losses are being paid by the customer, so they should be included in total boil-off budget.

Consider assessment of mitigation strategies for boil-off (in addition of what was presented in reviewer only slides). FY17 effort will address this.

Use of the HDSAM to perform analysis was selected because it was "directed by the program" according to the presenter. It seems, however, that this approach is backwards, and instead a complete analysis of the pathway should inform building the HDSAM model. We have an on-going relationship with ANL and changes to HDSAM can be made if needed.

Cryocompressed does not seem to be a realistic future pathway. Only a single OEM is on-board, collaborating. It is unclear why DOE funds are being allocated to this pathway. Cryo-compressed has many benefits, especially at large scale (large demand and large vehicle capacity). Although not considered for short term H<sub>2</sub> deployment (like some other DOE funded technologies...), cryo-compressed technology should be fully understood so that it is mature if/when limitations on current technologies are reached.

# Collaborations with Industry Leaders

- **Linde:** Very cooperative, sharing detailed information throughout pump development, construction, and installation. Interpreting and sharing data from multiple pumps, and on LH<sub>2</sub> deliveries.

# Risks/Challenges for FY17 milestones, Future work

- *Verify that LH<sub>2</sub> pathway code behaves as expected*
  - **Challenge:** Although the code looks appropriate to estimate losses during LH<sub>2</sub> transfer, a few modifications need to be made (2 phase EOS, top fill, subcooled...)
  - **Solution:** The code is being studied intensively and upgraded. We should know soon enough whether the code is appropriate.
- *Obtain park/drive/fill cycle patterns*
  - **Challenge:** We need to obtain parking duration and distance driven, per day, of a wide statically representative population, over a long period (week to month to year). As of now, we have not been able to secure the adequate source of data.
  - **Solutions :** On-going discussions with Cal Road Charge Pilot, reached out to UC Davis (STEPS, Dr. Nicholas). Hopeful sets of data from EV effort may be available.

Critical challenges are being addressed early in the project

# Summary: LLNL will develop and exercise models to simulate boil-off losses from plant to car for LH<sub>2</sub> pathway, propose mitigation solutions

## Relevance

LH<sub>2</sub> has great benefits for large scale(s) hydrogen deployment (cost, logistics, safety..), better understanding of losses is necessary

## Approach

Simulate losses mechanisms along the LH<sub>2</sub> pathway (transfer and boil-off : liquefaction plant -> trailer -> station Dewar -> pump -> cryo-compressed car), using real gas EOS and 2 phases, including statistical approach for variety of park/drive/fill scenarios

## FY17 Progress

Project just started (3 months)  
Simulation framework is being modified  
Driving scenarios are being collected

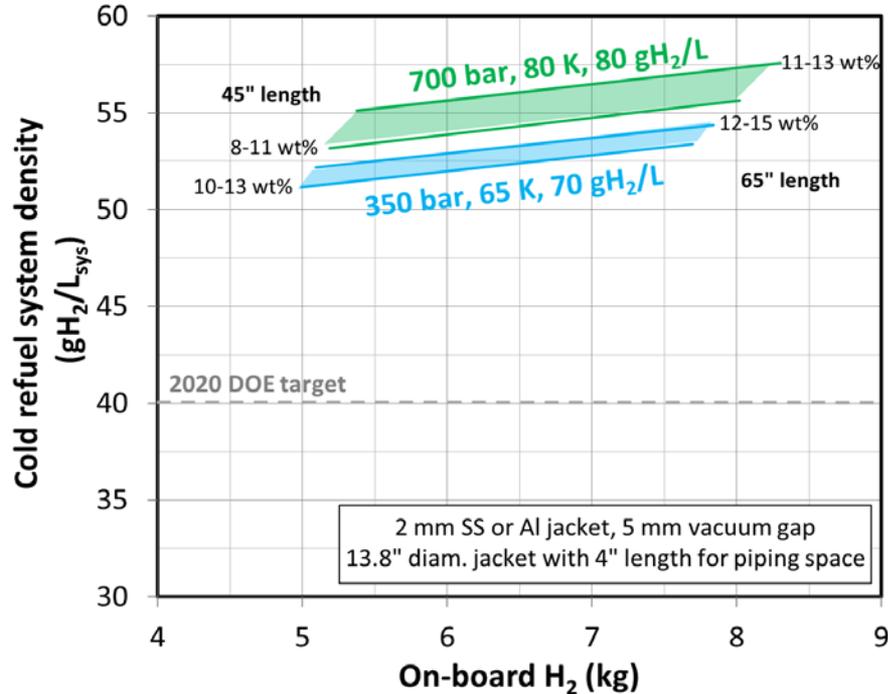
## Future work

Verify thermodynamics codes (pathway + park/drive/fill)  
Run typical cases  
Propose mitigating procedures/technologies

# **Technical back-up slides**

# Cryogenic H<sub>2</sub> offers rapidly refueled storage with volume, capacity, & safety advantages that outweigh technical challenges

- High density (cryo) H<sub>2</sub> allows minimum vessel volume & mass per kg H<sub>2</sub>, thus *minimum* cost
- Min burst energy @ refueling, high on-road safety factor (5-10), inert secondary containment
- Integrated with large scale LH<sub>2</sub> pathway, low station footprint (100+ kg/hour, < 1.5 kWh<sub>e</sub>/kg)



7 minute 10 kgH<sub>2</sub> fill to 70 g/L (350 bar, 65 K)

## Challenges for the technology:

- *Compact* vacuum jacket necessary for system density
- Need both minimum heat transfer (parking) *AND* strong suspension (driving)
- Temperature *variations* alter material properties, density, dormancy, H<sub>2</sub> burst energy

Projections: 5 kg H<sub>2</sub> system at 700 bar with 9+ wt% & 50 g/L

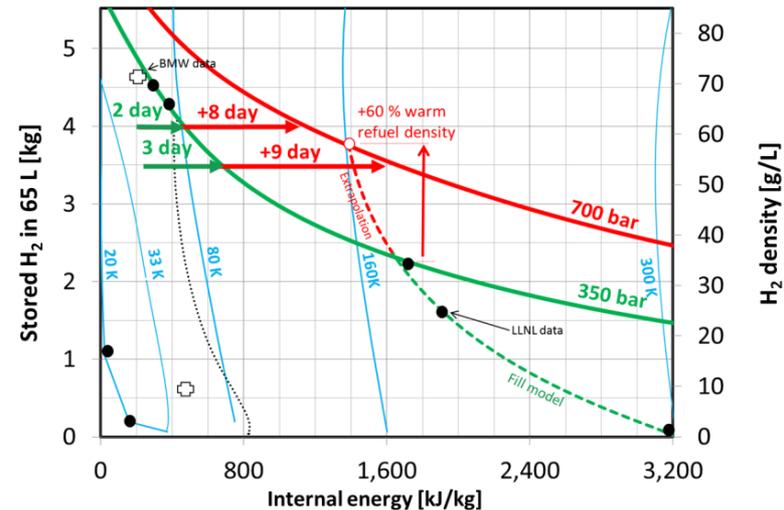
# Technical challenges for cryo-compressed H<sub>2</sub> storage

*Cryogenic durability of Type III composite pressure vessels, especially for the liner, is unknown*

- Other project addressing this by building & cycle testing specifically designed Type III vessels.
- Cryogenic durability is aided by improved material properties at low temperatures:  
Metal: Increased yield and ultimate stress. Fiber: increased stiffness.

*Driving range inconsistency due to cryogenic refueling might not be acceptable for the driver*

- Driving range remains constant once driving habits are established and maintained.
- Driving range is self-regulated:
  - Frequent use maintains the vessel cold and enables high density refueling
  - Infrequent use warms up vessel and reduces fill density, avoiding fuel venting
- Higher pressure helps reduce driving range variations



*The composite of the vessel outgasses over time, reducing the performance of the insulation*

- Preliminary results show that cryogenic temperatures reduce outgassing (“cryo-pumping”)
- It is still critical to demonstrate a long-term solution to vacuum stability
- We have proposed a promising approach and look forward to demonstrating its feasibility

# Approach (task 2): Cryo-compressed vehicles have a very dynamic behavior in terms of Temperature, Pressure and Capacity

